Theoretical Study of Ligand Exchange Reaction on Bis(Imido) Uranium(VI)

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For the past 150 years, studies of uranium(VI) have been generally directed towards understanding the chemical behavior and unique bonding in the uranyl ion (UO_2^{2+}). This ion possesses U-O bonds that have high thermodynamic stability and extreme kinetic inertness. As a result, the majority of UO_2^{2+} reaction chemistry involves substitution of equatorially coordinated ligands while leaving the U-O bond unaffected [1]. Recently, we have reported the syntheses of isoelectronic bis(imido) $[U(NR)_2]^{2+}$ and oxo-imido $[U(NR)(O)]^{2+}$ ions that possess many of the bonding features found in UO_2^{2+} [2].

Here we report investigations of the reactivity of the $[U(NtBu)_2]^{2+}$ (Fig. 1.) ion towards aryl isocyanates. Given the strength and stability of the U=O multiple bond, these reactions were anticipated to produce the oxo-imido framework. Instead, we observed an unexpected reaction that does not involve U=O bond formation, but rather an imido exchange reaction in which aryl-imido for alkyl-imido substitution occurs.

Stirring orange-red solutions of **1** with PhNCO in CH_2Cl_2 generates dark red-brown solutions. In the reaction with PhNCO, the mixed bis(imido) complex, $U(NPh)(N^tBu)(I)_2(OPPh_3)_2$ (**3**), can be isolated from this reaction, a complex that can be well characterized via ^1H NMR and crystallography (Fig. 2). While there is precedence for this aryl- for alkyl-imido substitution, it is not clear why this reaction does not form a thermodynamically and kinetically stable U=O bond. To provide some insight on why this exchange does not produce a U=O bond, density functional theory (DFT) calculations were performed to elucidate the relative energies of the intermediates and products of this reaction. There are two reaction pathways which could generate the bis(imido) product **3** and the oxo-imido species **2** from $U(N^tBu)_2(I)_2(OPPh_3)_2$ (Paths 1 and 2, Fig. 1). The first pathway involves the [2+2] cycloaddition of the C=N bond of the aryl isocyanate to form an N,N-bound ureato intermediate (**7**), which can isomerize to form species **8** with the –NPh group trans to the *tert*-butyl imido moiety. Compound **8** can then eliminate

tert-butyl isocyanate to generate the unsymmetrical bis(imido) complex **3** (Path 1). Alternatively, *N,O*-bound carbamate intermediates **9** and **10** could form, which result from the [2+2] cycloaddition of the C=O bond of the aryl isocyanate across the U=N imido bond. Elimination of a substituted carbodiimide would generate the oxo-imido complex **2** (Path 2).

The computational results suggest the lowest energy pathway involves the [2+2] cycloaddition of the C=N bond of phenyl isocyanate to form the N,N-bound ureato intermediate **7** (Path 1, Fig. 3). In the calculations performed, it is assumed that $OPPh_3$ dissociation occurs in order to generate intermediates **7** and **8**. Experimentally, the reactions between **1** and PhNCO proceed much more slowly in the presence of excess OPPh3, as is consistent with this assumption. Overall the transformation of $U(N^tBu)_2(I)_2(OPPh_3)_2$ (**1**) to $U(NPh)(N^tBu)(I)_2(OPPh_3)_2$ (**3**) is exergonic, with the free energy of the bis(tert-butyl)imido uranium complex (**1**) + PhNCO higher than the mixed imido species **3** + ^tBuNCO by 5.6 kcal/mol.

In contrast to this mechanism, the calculated [2+2] C=O cycloaddition bond pathway (Path 2) involves the formation of the higher energy *N,O*-bound ureato intermediates **9** (19.8 kcal mol^{-1}) and 10 (28.7 kcal mol^{-1}). Complex **9** can then eliminate the mixed carbodiimide $^tBuN=C=NPh$ and form the oxo-imido species **2**. As anticipated, the relative energy of **2** is substantially lower in energy than the unsymmetrical imido species **3** (15.2 kcal/mol). This energy difference between U=O and U=N bond formation has also been observed in cyclopentadienyl-substituted uranium(IV) complexes.

Given the difference in the relative energies of the intermediates between these two pathways and the results from ^{15}N-labeling studies, it appears the mechanism for the formation of **3** involves the [2+2] cycloaddition of the aryl isocyanate C=N bond across the U=N imido moiety. These results are quite surprising given the thermodynamic and kinetic stability of U=O bonds. However, the experiment repeated with labeled ^{15}N supports the proposed exchange reaction mechanism.

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[1] J.J.M. Katz and G.T. Seaborg, in *The Chemistry of the Actinide Elements,* 2nd ed., Chapman and Hall: London, 1137-1140 (1986).
[2] T.W. Hayton et al., *Science,* **310,** 1941 (2005).
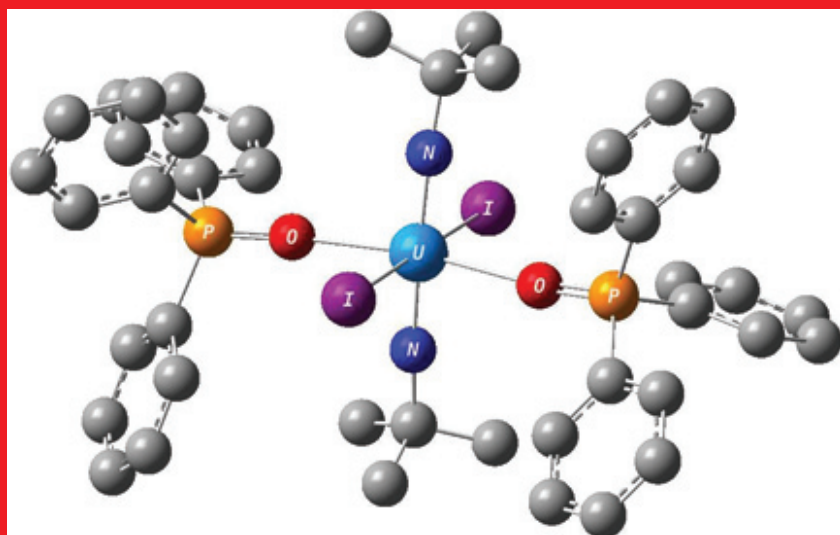
Fig. 1. Molecular structure of [U(NPh)₂(NᵗBu)I₂(OPPh₃)₂](1):
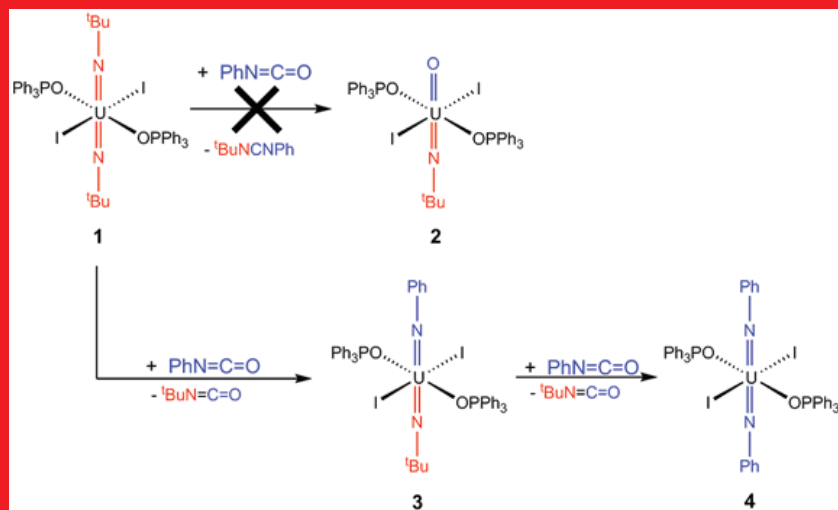*U-N=1.850Å, U-O=2.408Å, UI=3.169Å, O-P=1.528Å, N-U-N=175 deg.*

Fig. 2. Given the strength of U=O bonds, it was anticipated that the reaction of the bis(imido) complex U(NᵗBu)₂(I)₂(OPPh₃)₂ (11) with aryl isocyanates would yield the oxo-imido complex 2 or possibly an N,O-bound ureate.
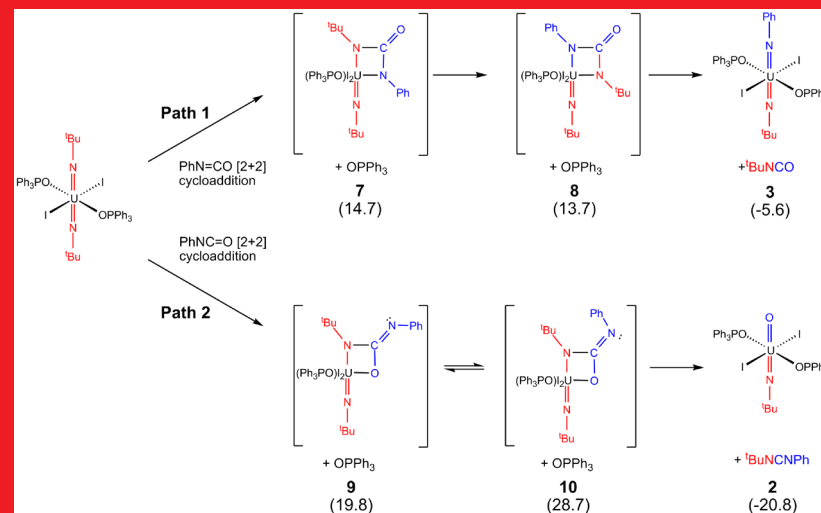

Fig. 3. Relative free energies of the products and intermediates in the potential pathways for the formation of 2 and 3. Energies reported at the hybrid DFT level of theory relative to the energy of 1 are provided in parentheses in kcal/mol.